UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYPYRROLE/MONTMORILLONITE CLAY CONDUCTING POLYMER

FARIZ BIN ADZMI

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PREPARATION AND CHARACTERIZATION OF POLYPYRROLE/MONTMORILLONITE CLAY CONDUCTING POLYMER

By

FARIZ BIN ADZMI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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Abstract of thesis to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF POLYPYRROLE/MONTMORILLONITE CLAY CONDUCTING POLYMER

By

FARIZ BIN ADZMI

January 2007

Chairman: **Professor Anuar Kassim, PhD**

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In this study, Ppy/MMT nanocomposites have been prepared by polymerization of pyrrole in the presence of $FeCl_3$ as oxidation agent and MMT clay in aqueous medium through the chemical polymerization.

The electrical conductivity of the Ppy/MMT nanocomposites was measured by using four-point probe technique. Conductivity of the Ppy/MMT nanocomposites increased from 0.45 to 2.25 S/cm. The increase of conductivity depended on the percentages of Ppy loading in the nanocomposites. Ppy/MMT nanocomposites exhibited similar infra-red (IR) absorption peaks as Ppy and MMT clay. Thereby, confirming the presence of the Ppy and MMT in the products. The X-Ray Diffraction (XRD) patterns revealed, MMT strong peak at $2\theta = 6.68^{o}$ (*d*-spacing 13.22 Å) and for Ppy/MMT nanocomposites is at $2\theta = 4.92^{o}$ (*d*-spacing 17.94 Å). The shifting of the angle 2θ is indicated that the insertion of Ppy has occurred. As determined from XRD analyses the crystalline size of MMT is 17.31 Å and is 25.42 Å for Ppy/MMT nanocomposites.

Thermal gravimetric analysis (TGA) revealed the improvement of degradation temperature of Ppy is at 157.36 to 177.21 ºC for Ppy/MMT nanocomposites. Scanning electron micrographs (SEM) revealed some interesting morphological differences between the pure MMT clay and Ppy/MMT nanocomposites. The Ppy/MMT nanocomposite exhibits a denser and more compact morphology. Particle formation of irregular and smaller size was clearly revealed by SEM.

The effects of several parameters in producing Ppy/MMT nanocomposites were also studied. When percentage of MMT was increased from 1 to 7% the conductivity was decreased from 2.25 to 0.38 S/cm. Result shows higher conductivity for sample prepared at low temperature (~5ºC) compared to room temperature (25ºC). The surface morphology of the Ppy/MMT nanocomposites at low temperature is more compact and denser compared to Ppy/MMT nanocomposites prepared at room temperature. $FeCl_3$ is the suitable oxidation agent to produce Ppy/MMT nanocomposites in aqueous medium. While 6 hours is the suitable preparation time for completion of polymerization of pyrrole.

Abstrak yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN TERHADAP POLIPIROL/MONTMORILLONITE KLAY POLIMER PENGALIR

Oleh

FARIZ BIN ADZMI

Januari 2007

Pengerusi: **Professor Anuar Kassim, PhD**

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Dalam kajian ini, Ppy/MMT nanokomposit telah dihasilkan melalui proses pempolimeran pirol dengan menggunakan $FeCl_3$ sebagai agen pengoksidaan dan MMT klay dalam larutan akueus melalui proses pempolimeran kimia.

Keberaliran elektrik bahan Ppy/MMT nanokomposit ini diukur menggunakan teknik prob empat titik. Didapati keberaliran bahan nanokomposit ini bertambah daripada 0.45 kepada 2.25 S/cm. Pertambahan keberaliran ini bergantung kepada peratusan polipirol masuk ke dalam bahan Ppy/MMT nanokomposit. Ppy/MMT nanokomposit menunjukkan penyerapan sinar infra merah (IR) sama dengan penyerapan di dalam polipirol dan MMT klay. Ini membuktikan kewujudan polipirol dan MMT klay di dalam Ppy/MMT nanokomposit. Paten pembelauan sinar-X (XRD) menunjukkan puncak penyerapan tajam MMT klay pada $2\theta = 6.68^\circ$ (jarak-*d* 13.22 Å). Manakala bagi Ppy/MMT pada pada $2\theta = 4.92^\circ$ (jarak-*d* 17.94 Å). Perubahan pada sudut 2θ

menunjukkan kemasukkan polimer polipirol ke dalam dalam MMT klay. Saiz hablur untuk MMT adalah 19.31 Å, manakala untuk Ppy/MMT nanokomposit adalah 25.42Å. Analisis terma gravimetri (TGA) telah menunjukkan peningkatan suhu degradasi daripada 157.36ºC untuk polipirol kepada 177.21ºC untuk Ppy/MMT nanokomposit. Analisis mikroskop pengimbas electron (SEM) menunjukkan keadaan permukaan yang berbeza diantara MMT and Ppy/MMT nanokomposit. Ia telah menujukkan permukaan Ppy/MMT nanokomposit adalah padat dan rapat. Formasi partikel adalah tidak sekata dan bersaiz kecil dapat dilihat dengan jelas.

Kajian ini juga mengkaji kesan-kesan dan faktor-faktor lain yang mempengaruhi penghasilan Ppy/MMT nanokomposit. Apabila peratusan MMT ditingkatkan daripada 1 kepada 7% didapati keberaliran Ppy/MMT nanokomposit semakin menurun daripada 2.25 kepada 0.38 S/cm. Kajian menunjukkan keberaliran pasa suhu rendah (~5ºC) adalah lebih tinggi darapada suhu bilik (25ºC). Perbezaan juga terdapat dalam morfologi permukaan Ppy/MMT nanokomposit di mana pada suhu rendah permukaan Ppy/MMT nanokomposit menjadi semakin padat dan rapat. Seterusnya $FeCl_3$ adalah agen pengoksidaan yang paling sesuai digunakan untuk penghasilan Ppy/MMT dalam medium akueus. Sementara 6 jam adalah masa yang sesuai untuk melengkapkan proses pempolimeran pirol.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the supervisory committee are follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that is has not been previously or concurrently submitted for any degree at UPM or other institutions.

FARIZ BIN ADZMI
Date: 23 April 2007

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LIST OF ABBREVIATIONS

ASAP	Analysis of surface area and porosity
ATBN	Acrylonitrile copolymer
BNSA	5-buthylnaphthalene
CSA	Camphor sulfonic acid
D/M	Dopant/monomer
DMAC	Dimethylacemide
FTIR	Fourier transfer infrared spectroscopy
MBSA	ρ-methylbenzenes sulfonic acid
MMT	Montmorillonite
NaANS	Sodium alkylnaphthalene sulfonate
NaDES	Sodium alkylsulfonate
NSA	β-naphthalene
O/M	Oxidant/monomer
Ppy	Polypyrrole
Ppy/MMT	Polypyrrole/montmorillonite nanocomposites
PTS	Polytoluene sulfonic
RIA	Relative humidity
SEM	Scanning electron microscopy
T_g	Glass transition temperature
TGA	Thermal gravimetric analyses
XRD	X-ray diffraction spectroscopy
ESR	Electron spin resonance

VRH	Variable range hopping

CHAPTER I

INTRODUCTION

Background

Since their discovery in the mid-1970's, conducting polymers have been a hot research area for many academic institutions. This research has supported the industrial development of conducting polymer products and provided the fundamental understanding of the chemistry, physics and materials science of these materials. The impact of the field on science in general was recognized in 2000 by the awarding of Nobel Prize for Chemistry to the three discoverer of conducting polymer: Alan MacDiarmid, Alan Heeger and Hiderki Shirakawa.

A research over the past 25 years shows the levels of publications increasing rapidly after 1980 (Figure 1). The data suggest a peak in patenting in the late 1980's, while the rate of scientific publications increases unabated through the end of the 1990's. At the present time, around 40 new journal articles related to the conducting polymer are published every week.

Figure 2 shows the main areas of interest of the paper published on conducting polymer. With almost half of the publications related to the synthesis of conducting polymer. The next largest area of research has been into the physic conduction mechanism, while application for conducting polymer account for fewer than 20% of publication.

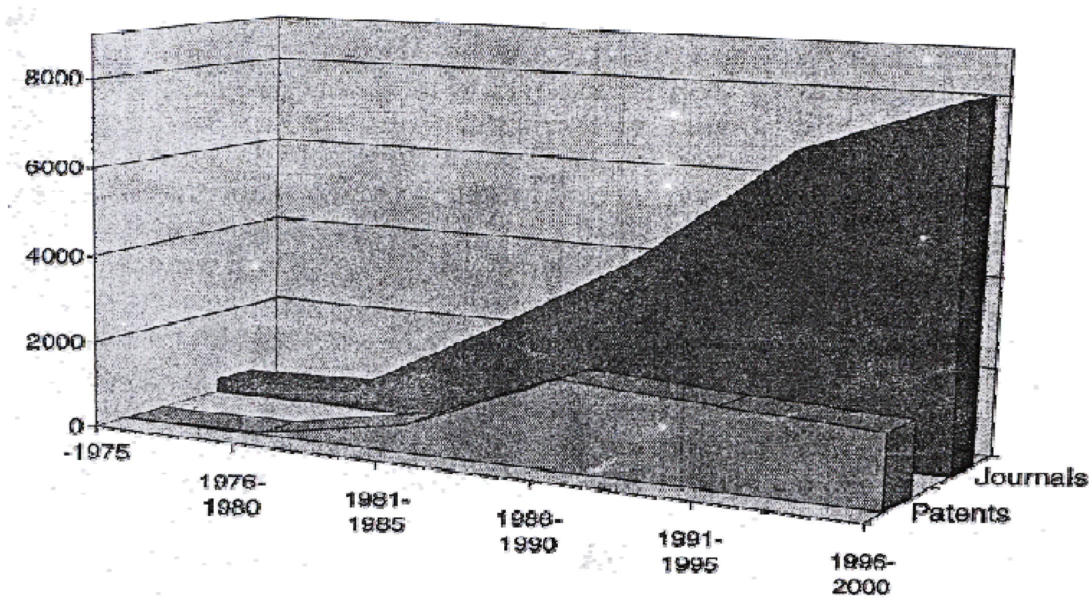


Figure 1: Number of scientific papers published and patents issued in the area of conducting polymers for the past 25 years (Gordon *et al*., 2003).

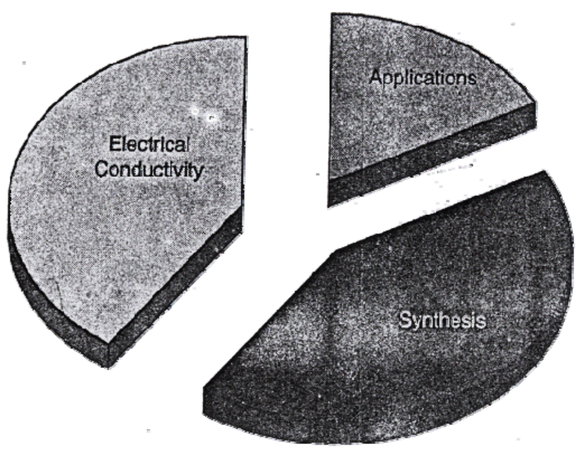


Figure 2: Scientific papers published on conducting polymers in the last 10 tears categorized into various topics (Gordon *et al*., 2003).

Conducting Polymer

It is possible to create conducting polymers with a diverse range of properties. For example, chemical properties can be manipulated to produce materials capable of trapping simple anions or to render them bioactive. Electrical properties can also be manipulated to produce materials with different conductivities and different redox properties. After synthesis, the properties of these fascinating structures can be manipulated further through redox processes. The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties in conducting polymers. These complex properties can be controlled only if we understand, first the nature of processes that regulate them during the synthesis of the conducting polymers, and second, the extent to which these properties are changed by the application of an electrical stimulus.

Conducting polymers have emerged as one of most popular in materials science research. It has all the desirable properties:

- They are readily engineered at the molecular level to recognize specific stimuli.
- Because they are conductive, they are facilitating transport of electrical information.

A wide range of conducting polymers is shown in Table 1.

Conducting polymers are of class of materials that are, no doubt, destined to play a major role in intelligent materials science. As outlined in the reminder of this text, the properties of these materials are versatile.

Table 1: Typical conducting polymer structures.

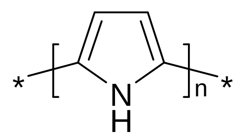
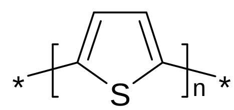
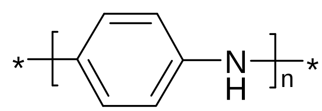
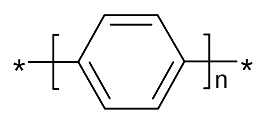
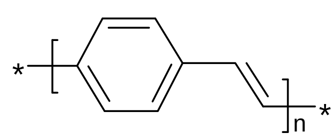
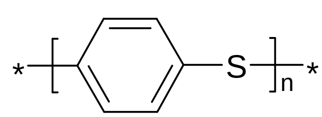
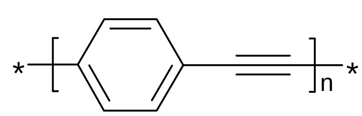
Name	Structure
Polypyrrole (Ppy)	
Polythiophene (PTh)	
Polyaniline (PAn)	
Poly(para-phenylene) (PPP)	
Poly(phenylene-vinylene) (PPV)	
Poly(phenylenesulfide) (PPP)	
Poly(phenylene ethylene) (PPE)	

Table 2 shows the properties of conducting polymer and their behavior that can be manipulated *in situ* using appropriate electronic stimuli.

Table 2: Property changes typically observed upon electrical stimulation to switch conducting polymer between oxidized and reduced states.

Property	Typical Change	Potential Application
Conductivity	From 10^{-7} to 10^{3} S/cm	Electronic components, Sensors
Volume	3%	Electromechanical actuators
Color	300-nm shift in absorbance band	Displays, smart windows
Mechanical	Ductile-brittle transition	
Ion permeability	From zero to 10^{-8} $molcm^{-2}s^{-1}$ in solution	Membranes

Problems Statement

Poor processibility of polypyrrole (Ppy) due to its insolubility and infusibility has retarded further investigation on the structure and structure-physical properties. To improve the processibility, many researches have been engaged in the development of soluble or swollen Ppy and dispersible fine-powdered Ppy. At the same time, the electric properties and/or stability of chemically prepared Ppy have also been investigated at many laboratories because the stability of conducting polymers seems to be the main limiting factor in their practical applications.

In recent years, composites of a special category, terms "*nanocomposites*" have been studied with growing interest. For example Ppy base zeolite and Ppy base alumina nanocomposites have extensively study due to improve the processibility of the Ppy and enhance the mechanical properties of Ppy (Zhang *et al.*, 1997).

In this presence of study the Ppy/MMT nanocomposites has been prepared through the chemical polymerization by using $FeCl_3$ as the oxidation agent for polymerization of pyrrole in aqueous medium. The nanocomposites prepared are characterized in chemical and physical properties.

Objectives of the Study

This thesis presents and discusses the result of series experimental and analyses study of physical and chemical characteristic of polypyrrole/montmorillonite (Ppy/MMT) nanocomposites.

To achieve this aim, the following objectives are proposed:

1. To prepare and characterize the Ppy/MMT nanocomposites.
2. To study the effect of parameter such as concentration of pyrrole and $FeCl_3$, increasing percentage of MMT, oxidant used, preparation temperature and time of preparation on Ppy/MMT nanocomposites.